

REPORT DOCUMENTATION PAGEForm Approved
OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 10/01/04	3. REPORT TYPE AND DATES COVERED final: 4/15/03-12/14/03
4. TITLE AND SUBTITLE Tools for Condensed Phase Computational Chemistry		5. FUNDING NUMBERS DAAD19-03-1-061 DAAD19-03-1-0061	
6. AUTHOR(S) Krzysztof Szalewicz		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Delaware Newark, DE 19716		10. SPONSORING / MONITORING AGENCY REPORT NUMBER 45238.1-CH-CF	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The workshop developed recommendations for those computational chemistry tools best suited to attack research problems in properties of energetic molecules – individually and in condensed phases. A small, international group of experts presented their work and discussed current tools of computational chemistry in the context of the Army program of energetic material design. These experts, chosen for their specific skills, came from Europe and the US.			
14. SUBJECT TERMS computational chemistry condensed phase of energetic materials			15. NUMBER OF PAGES 19
			16. PRICE CODE
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. Z39-18
298-102

ARO Report

Tools for Condensed Phase Computational Chemistry

An Army/University of Delaware Workshop held at

Clayton Hall, Newark, Delaware

27-30 May 2003

Organizers:

Prof. Krzysztof Szalewicz, Department of Physics, University of Delaware

Dr. Robert W. Shaw, Chemical Sciences, Army Research Office

Abstract:

This workshop brought international experts on condensed phase computational chemistry codes together with Army scientists working on energetic materials to help ensure that Army scientists have available the best current computational tools (codes). The workshop was planned by U Delaware, ARO, and ARL-WMRD.

This workshop report is a guide for the Army research program in energetic material design. New research collaborations between Army scientists and experts at the workshop are likely and ongoing collaborations were improved.

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Description of the Workshop: Tools for Condensed Phase Computational Chemistry

The workshop developed recommendations for those computational chemistry tools best suited to attack research problems in properties of energetic molecules – individually and in condensed phases. A small, international group of experts presented their work and discussed current tools of computational chemistry in the context of the Army program of energetic material design. These experts (see Participants List), chosen for their specific skills, came from Europe and the US.

The workshop emphasized problems that can be treated now. To facilitate discussion, we described the tools as falling into three groups:

1. Readily available, widely used, relatively friendly packages, e.g., MolPac, Gaussian, Cerius suite
2. Available, but directed to the specialist, require special training, e.g., DMAREL
3. Written and used within a research group, accessible only to a few.

Questions raised included: What tools are best suited to current Army computational problems? What investment (time, money) is required to use these tools? How can the tools output be validated (what experiments)?

The workshop began with Army scientists (Betsy Rice, Cary Chabalowski, William Mattson) describing their current goals and problems. These included predictions of crystal structures and other physical properties of energetic molecules. Visiting experts came from academia (University College-London, Cambridge University, Imperial College, Rice University, UCLA, Mississippi State University, and Universities of Illinois, Delaware, and Maryland), Naval Research Lab, Pacific Northwest Lab, and NIST. These visiting experts described capabilities of current computational chemistry codes.

All these presentations included time for questions and discussion. Following the presentations, the participants divided into groups led by Army scientists to discuss which packages would best suit current Army projects and what research should be done to develop these packages to enable future Army projects in design of energetic materials. At the end, these discussions were summarized and discussed by everyone. This report includes those summaries.

The workshop scientific sessions and meals were held at the Clayton Hall Conference Center. Participants all lodged in the same hotel (Embassy Suites) to enhance opportunities for discussion.

Previous Army Statements of Interest

The discussions were based, in part, on questions raised at the ARO/ARL/ARDEC 2000 EM Planning Meeting. Some specific questions follow.

Computational Chemistry and Properties of Energetic Molecules

Question: What theoretical tools are most important?

Answer: We need reliable force fields (many body forces) to model chemical reactions in the

condensed phase.

Computation requirements for the condensed phase are large because we must include many molecules (many body problem). Often these condensed phase calculations rely on periodicity in the structure to reduce computation time. But chemical reactions break this order.

We should move our methods to determine low-energy crystal structures of energetic materials from classical molecular packing to quantum mechanical molecular packing. This project may be appropriate for a graduate student thesis.

Screening Tools: We want to use theory to screen notional materials (molecules that may not have been synthesized but which, based on their expected structures, appear to have good properties). The first properties we want to predict are: burning rate, heats of formation, densities.

Density: Molecular packing calculations are the best method for predicting densities of new solid materials. One must generate a variety of crystals corresponding to the various crystalline space groups from the coordinates of a single molecule. Each crystal must be optimized (the crystallographic parameters are minimized with respect to energy, while the molecular parameters themselves remain fixed) and all energies are compared. The current criterion for selection of the most probable structure is lattice energy; i.e., the structure that has the lowest lattice energy is assumed to be the "correct" crystal structure. This criterion has proven to be insufficient and additional criteria, perhaps the evaluation of ΔG for each crystal structure, should be included in the selection procedure.

Additional improvements to such calculations would be improved intermolecular interaction potentials, and relaxation of the rigid molecule assumption to partial deformation of the molecules (inclusion of torsional rotations for example). Although molecules like RDX may be adequately modeled as rigid structures, allowance for molecular deformation will likely be especially important for floppy molecules like PETN. So we should consider a stepwise approach: optimize ΔG (requiring calculation of the energy second derivatives of the crystals, very time consuming) and allow some intramolecular motion.

All calculations discussed to date are classical; hence they require an intermolecular force field. And, as mentioned above, do not include intra-molecular dynamics. The energetic molecule intramolecular potential developed by Sorescu, Rice, and Thompson (1) has successfully matched experimental crystallographic structures and lattice energies for a variety of explosives. However, the force field was tested by generating the crystal structure of RDX assuming the experimentally determined space group, and doing an energy minimization. These results give crystal structures in good agreement with experiment. Thus, predictions of densities are good. It may be, however, that the force field, in the absence of space group information, would predict other crystal structures with more favorable ΔG . To truly test the force field, one must pack RDX, for example, in every possible fashion according to the 230 crystalline space groups and find the best ΔG . To have confidence in the force field, it must generate the correct crystalline space group without reliance on experiment at all.

1 J. Phys Chem A, 103, 989-998, 1999

Summary by Focus Group 1
(reported by Cary Chabalowski, Ed Byrd, William Mattson)

The discussion session was divided into two general topics:

What do we need to do to predict sufficiently accurate crystal densities and other static properties? (At least better than what is currently available).

What do we need to predict the chemistry of detonation in the solid state? Along with this, we asked that both short-term and long-term goals be put forth in terms of modeling developments.

Comments:

When we refer to optimizing crystal structures, we mean the ability to optimize both cell parameters and atomic positions. PBC stands for periodic boundary conditions.

TOPIC #1: Crystal Densities

This question seemed to evolve into discussions on methods for predicting the complete van der Waals forces. There was also discussion on sampling configuration space. Some of the recent work by Mark Tuckerman may be of interest here (conformational sampling algorithms).

1.A Force-Field Approach

The currently used methods of predicting crystal structure are based on the use of (mostly empirical) force fields. The discussion concentrated on possible applications of non-empirical methods to develop such force fields.

Asymptotic force fields:

Not many new ideas were proposed on the topic of predicting accurate electrostatic intermolecular interactions, since a general sense prevailed that currently existing, or soon-to-be developed, Density Functional Theory (DFT) functionals will be sufficiently accurate to give good asymptotic electrostatic, induction (polarization), and dispersion interaction energies. The latter may sound as going against the common knowledge, but is true if time-dependent DFT (TD-DFT) is used to calculate the dynamic polarizabilities, see below. However, some discussion did occur.

Force-fields including overlap and exchange effects:

In order to calculate the force fields in the region of the van der Waals minimum, critical for determining the crystal structure, one has to include the overlap (charge penetration) and exchange effects. The overlap effects significantly change the values of the electrostatic, induction, and dispersion forces in this region and the exchange energies, providing the repulsive forces, are responsible for the very existence of van der Waals minima.

(LONG-TERM GOAL for supermolecular DFT methods)

Due to its efficiency, the DFT method would potentially enable calculations of interaction force fields for molecules typical for energetic materials. Unfortunately, current exchange-correlation DFT functionals have shown mixed results in predicting accurate electrostatic and induction interactions with charge-penetration effects (as discussed in Szalewicz's talk), including hydrogen bonding. It is believed to be due to the fact that asymptotic corrections (AC), fixing up the electron density at large distances from the center of a molecule, have not been applied (see below). Actually, it is not even clear how to apply these corrections in supermolecular approach. In any case, a more serious failure of DFT is in recovering the dispersion energy (see below). However, the asymptotic electrostatic and induction energies, depending only on molecules' multipole moments and static polarizabilities, are predicted well by the modern DFT even without AC. Thus, for small and very polar molecules, whose interactions are dominated by the asymptotic electrostatics and induction, supermolecular DFT approach may give reasonable predictions. Such predictions will be further improved by ongoing research into the development of better DFT functionals, independent of any specific work on developing better solid state modeling methods. Using supermolecular DFT to deal with general-case van der Waals forces is totally an open issue and an unsolved problem. Several groups investigate this problem but it is impossible to say when and if a solution will be found.

(SHORT-TERM GOALS for building non-empirical force fields)

One possible method for obtaining accurate electrostatic, induction, and exchange interaction energies valid at all intermolecular separations is through the use of a newly developed version of Jeziorski-Szalewicz's Symmetry Adapted Perturbation Theory (SAPT), which is based upon the use of the Kohn-Sham (KS) orbitals from noninteracting monomers in the SAPT expansion, as proposed by Williams and Chabalowski. This approach, referred to as SAPT(KS), when used with asymptotically corrected functionals, gave electrostatic, induction, and exchange interaction energies for dimers that compared to within a few percent of benchmark traditional SAPT calculations, but at a much reduced computational cost. The size of the monomers that can be treated is yet to be determined, but Szalewicz thought that a dimer of RDX could be studied in near future. The remaining component of the interaction energy, the dispersion force, can also be accurately computed using SAPT based on TD-DFT dynamic polarizabilities. These dimer interaction energies can be used in a fitting procedure to create non-empirical force fields to be used in modeling of molecular crystals. These energies can also be used to improve the individual potential energy terms in analytical empirical force fields, as discussed in the next subsection.

Empirical Force Fields:

(SHORT TERM GOAL)

If reliable fitting data is available through either experiment or theory [SAPT(KS) was specifically mentioned], it was suggested that classical force field packages (e.g. DMAREL from Price), could and would be improved by refitting using fitting codes such as GULP. There was a general sense that these force field approaches were capable, in general, of reproducing the electrostatic

interactions in crystals to an acceptable accuracy provided that accurate multipole moments are known. Some discussion ensued about the need for including an effective anisotropic partial charge distribution, or an equivalent multipole expansion of the charge, around atoms or groups, allowing for interactions such as those involving an electron lone-pair. The need to include other refinements was also discussed, such as polarizable charge distributions or multipole expansions of the charge. However, these refinements are probably less important than the inclusion of a better representation of the remaining components of the interaction energy like dispersion or exchange.

In this spirit, Murdachaew suggested a specific approach to developing a force field including dispersion and other interaction terms based on Szalewicz's SAPT. The *ab initio* SAPT energies can be used to produce first-principles force fields. These energies are fed directly into a fitting code developed by Robert Bukowski (in Szalewicz's group). This code uses asymptotic van der Waals constants computed *ab initio* with the POLCOR code developed in Paul Wormer's group in Nijmegen). The resulting force field produces force fields with accurate asymptotic expansions that include the terms containing the C_6 through C_{12} coefficients. These coefficients or the monomer properties underlying them can be used to improve empirical force fields. The monomer properties can also be computed.

Krzysztof Szalewicz comments: What Garold Murdacheaw proposed makes a lot of sense. In fact, I had a long discussion with Sally Price after the conference and I suggested to her something similar (not knowing about Garold's suggestion). They should be able to investigate quite large molecules using a much better asymptotics than they do now, basically following our approach to asymptotics. Notice that in this way the asymptotic dispersion interaction, which is included only in a very crude way in current empirical force fields, will be very well accounted for. Furthermore, they could improve the exchange by utilizing the approximate proportionality of exchange to overlap effects. We are now using this approach for flexible-monomer potentials, but Sally Price with Richard Wheatley actually pioneered it.

(LONG-TERM GOAL)

It was suggested that a large database (primarily calculated?) of intermolecular interaction energies, as well as other molecular properties, be established. Such data could be very useful in refining analytical force fields. The current database at NIST is an obvious effort in this direction, but for individual molecules, and should be expanded to include inter-molecular interaction energies versus structures. This data should be assessed and documented for its accuracy whenever possible, and made available to the research community in an easily searchable form.

Dispersion Forces

(SHORT-TERM GOAL)

One more alternative to developing force fields for molecular crystals is to use the Hartree-Fock SCF method which gives a good account of electrostatic, induction, and exchange energies and at the same time is about as fast as the DFT method. SCF does not include, however, any dispersion terms.

The latter energy is a pure correlation effect and therefore its calculation will always be much more time consuming. One possibility is to add the asymptotic dispersion to the SCF interaction energy, but the accuracy of this approach may not be high enough for crystal modeling. A better accuracy will be achieved by using the TD-DFT, also called Coupled Kohn-Sham (CKS) method, to calculate dynamic polarizabilities and apply them in the disp(CKS) method of Szalewicz to get dispersion interactions. More precisely, this approach utilizes closely related quantities, Frequency Dependent Density Susceptibilities (FDDs) as predicted by TD-DFT. The FDDs can then be used in a generalized Casimir-Polder expression for dispersion energy valid at any intermolecular separation, and coded such that the cost of computations scales as n^3 , where n is the number of molecular orbitals in a dimer calculation. This approach, again combined with asymptotically corrected functionals, was capable of predicting dispersion energies within a few percent of the benchmark SAPT calculations for dimers. While this approach was said to scale as n^3 , further computational efficiency might be possible.

(LONG-TERM GOAL for DFT dispersion)

Although the supermolecular DFT method is now known to give fairly large errors for the electrostatic, induction, and exchange components, the weakest element of this method is the dispersion energy. This is well known from the fact that for interactions of rare-gas atoms which are dominated by dispersion, DFT gives simply nonsensical results. Probably all the DFT exchange-correlation functionals include some portion of dispersion interactions (for example, there are dispersion interactions in the uniform electron gas, thus, even LSDA contains some dispersion), but not even the empirically fitted or hybrid functionals include it well. There have been intensive efforts to develop functionals that could account for dispersion interactions. Kohn in 1998 (and perhaps independently Lundquist) proposed to use Time Dependent (TD) DFT to calculate the C_6 and C_{12} coefficients and include them in the functional. This, however, constructs functionals usable only for that specific molecule and not a general functional.

Szalewicz comments: Indeed, all the papers claiming to have solved the DFT problems with dispersion interactions ended up in computing just the asymptotic C_n dispersion coefficients. However, this task has been de facto achieved earlier by all the DFT papers devoted to frequency-dependent polarizabilities since once these are known, computation of C_n from the Casimir-Polder asymptotic formula is trivial.

1.B Periodic Boundary Conditions Approach

Virtually all computational predictions for molecular crystals involving large organic molecules are obtained with force-field methods. The PBC approach where optimization of the lattice can be performed on the potential energy surface computed “on-the-fly” would offer some advantages, in particular where the relaxation of monomer structures is important. However, the general consensus was that no computationally feasible approach currently exists for predicting crystal cell structures using PBCs that give sufficiently accurate predictions of intermolecular dispersion interactions, including DFT.

MP2-PBC method

(LONG-TERM GOAL for crystal relaxations)

The MP2 based codes of Scuseria (the PBC code is available, the MP2-PBC is currently not available in Gaussian-03) will account for dispersive interactions in a PBC framework within the limit of the accuracy of MP2 theory. While MP2-PBC exists, it is still a fledgling code/theory, and requires work to fully develop and test. Unfortunately, at this time, there are no analytical gradients in G03 within the MP2-PBC approach, so minimum energy crystal structures cannot be readily determined. Scuseria said that he plans to code these gradients, but this will take time. Other concerns about the use of MP2 included the inability to handle metalization, wherein the band gap decreases to near zero. This is a fundamental weakness in the use of MP theory, which requires the use of band gap energies (virtual orbital energies in molecules), and it was not clear how to correct this problem. Another issue surrounding the use of MP2 was the computational efficiency. In principle, MP2 does not scale as well as DFT with respect to the number of electrons. Work needs to be done to improve computational efficiency to allow for applications to larger unit or supercells.

Emily Carter comments: The problem is that MP2 conventionally scales as n^5 and all the truncation tricks used by all of us doing reduced scaling cannot be used here because the whole point is to retain the long-range correlation to get the van der Waals forces right. So it is not clear at all how to make MP2 scale in a way that makes it tractable without messing up the long-range interactions you want to keep.

Meanwhile, Gustavo Scuseria states: Our MP2-PBC is linear scaling, it is the prefactor that is huge, so calculations are expensive. Even the HF-PBC is expensive. Work needs to be done to improve efficiency and computer implementation of the current approach, which is still in its infant stages.

(LONG-TERM GOAL)

The suggestion was made to develop DFT OEPs, V_{XC} , by optimizing the orbitals within an MP2 calculation. Apparently, the idea was to generate exchange-correlation operators that retained the capabilities to generate electron densities that reproduce the MP2-like van der Waals forces.

Emily Carter says: As far as I understand the OEP strategy, you still have to do the MP2 calculations (an n^5 process as we were just discussing) and then one derives the KS EP from that. And no one has figured out how to go from one of those EP's to derive new general functionals, as far as I know.

Corrections to force-fields

(SHORT-TERM GOAL)

Professor Doren states: One method that depends only on existing computational methodology is a systematic correction, based on *ab initio* calculations to the predictions of force-field methods. The calculation begins with a crystal supercell, constructed and optimized with the "best

available" force field approach. The force field is used to run a dynamics simulation, from which snapshots are taken to provide an ensemble of configuration space samples. *Ab initio* single-point energies for the sampled configurations can be calculated using either periodic MP2 (e.g., with G03), or by calculating interactions of a unit cell with a small number of neighbor cells using supermolecule MP2 (or possibly SAPT) methods. Using free energy perturbation, a suitable ensemble average over these configurations provides an *ab initio* correction to the free energy, including dispersion at the level of the *ab initio* calculation. The method has been applied successfully to liquid state solvation, where 50-100 configurations typically suffice for accurate corrections. Moreover, in cases where the *ab initio* calculations show that the force field model is inaccurate, the *ab initio* results can be used to refit the force field. Thus, the method provides both a test of the accuracy of force fields, and a correction to their predictions. The method can be readily implemented without new technical developments, and given a reasonable force field, the cost of configuration sampling is inherently lower than that of using an *ab initio* method for sampling.

Monte-Carlo methods

(LONG-TERM GOAL)

A more rigorous approach to phase space sampling was suggested by Martin in the form of improving Quantum Monte Carlo (MC) calculations. He expanded this idea by suggesting a correlated sampling combined with Diffusion MC. He stated that better correlated sampling is needed to converge van der Waals forces.

Embedding approach

(LONG-TERM GOAL)

The suggestion was made to pursue an embedding approach. A high-level QC method is embedded into a lower-level treatment, so dispersion is explicitly included within the "embedded" part of the model via QC. The remainder of the system still faces the same issues of accounting, in some suitable fashion, for the dispersive interactions. Some questions were raised concerning whether or not this type of approach could be used with PBCs, but the response seemed to be that it could.

Emily Carter adds: The only reason to think about doing this is to see if the dispersion calculated via MP2 embedded in a periodic background treated with DFT (something we can do today) gives a more accurate description than does MP2 on isolated dimers.

SAPT with PBC

(LONG-TERM GOAL)

One serious issue concerning SAPT is whether or not it can be formulated for use with periodic boundary conditions. There had been some behind-the-scenes discussions during the conference

between Scuseria and Szalewicz, resulting in the notion that this might be possible. After the conference, Szalewicz, in consultation with Bogumil Jeziorski from University of Warsaw, developed a strategy for such a case. This strategy build upon the existing SAPT approach for trimers which can be applied to larger clusters as well without new conceptual difficulties. The current SAPT approach analytically splits the interaction energy into pair interactions and nonadditive terms.

This would be difficult for larger clusters, but if the splitting is not preformed, the method may be practical and allows the use of PBC.

To define this method more precisely, consider a set of atoms or molecules in a cell. This cell does need to be particularly large, typical size used in DFT PBC calculations should be sufficient. However, the cell should contain several monomers. If we neglect all the terms in the Hamiltonian that describe interactions between the molecules, this defines our operator H_0 and the removed terms are the operator V . We solve the zeroth-order problem and build the perturbation theory on top of it, all with PBC. There may be some issues, hopefully solvable somehow, related to simultaneously imposing the permutational and translational symmetry. Like in the regular SAPT, the zeroth-order wave function is not fully antisymmetric under permutations of electrons. Therefore, "symmetry adaptation" used in the regular SAPT has to be performed here as well. This must be done in a way preserving translational symmetry of the crystal.

SAPT can also be developed to calculate interactions of a molecule with surface. One monomer is the surface, represented by a few layers of crystal molecules/atoms in a very large supercell. The other monomer is the single molecule in the same supercell. The supercell is repeated periodically in all directions. Then one can calculate the interaction of these two monomers using SAPT.

An alternative way Szalewicz can see to extend it to the bulk crystal is to assume a fairly large supercell with one of the molecules removed as one monomer. The other monomer would be a single molecule in the same supercell, placed in the position of the void in the first monomer. Again, PBC are imposed on supercell.

TOPIC #2: Chemistry of Detonation in the Solid State

Predicting accurate reaction pathways is still a cutting-edge research problem even for unimolecular reactions, let alone in crystals. However before discussing accuracy of methods, a question arose concerning the usefulness of minimum energy pathways in shock and detonation studies of energetic crystals: Are transition states for minimum energy paths useful in modeling shock and detonation, because the input energy from the shock wave might be so great as to raise the internal energy of the molecules far above the reaction threshold. If so, the atoms might not sense the transition states. True? False? TBD? For the same reason, is knowledge of the minimum energy pathway, in general, even useful?

Emily Carter notes: If one does not even characterize the pathways at zero K and zero P first, I don't see how one can have any idea how to characterize pathways at arbitrary T and P. I think it is

essential to map out the PES as much as one can, as a function of P, and then one can know how T may affect the pathways observed for a given P.

(SHORT-TERM GOAL)

On a positive note, assuming that current DFT functionals could accurately predict chemical reactions, there are already methods available to study aspects of shock and detonation. Solid state codes have already been used to simulate shock waves [we are assuming these are pseudopotential planewave codes?]. Shock waves have been simulated in many ways: the continuum level hydrodynamic approach (no input from atomistic level), from molecular dynamics simulation using analytic potential functions, and more recently by Carter and Ortiz using a multiscale finite element approach that takes input from DFT. The current methods also allow study of isotropic and anisotropic compressions, both in bimolecular systems and in crystals. High temperature Born-Oppenheimer Molecular Dynamics or Car-Parinello MD simulations can also be done (on a reasonable time scale – one must be careful here and check the time scale of the detonation wave. BOMD or CPMD calculations can be done for time of the order of ps but not ns) with today's methods. Another thought was to study aspects of detonation by simulating two molecules colliding with large kinetic energy.

Emily Carter states: Take it from someone who has done simple bimolecular collisions, one can look at representative trajectories but you will not, with *ab initio* MD, be able to do enough statistics to really sample phase space.

(LONG-TERM GOAL)

But once again, the accuracy of DFT theory, or more appropriately the existing exchange-correlation functionals, was said to be unreliable in predicting accurate transition state (TS) structures and energies, including the possibility of representing unrealistic electronic spin states along the reaction paths. What can we do to improve the functionals at the TS, and insure that the densities represent the correct spin state of the system at all points along a reaction path?

Emily Carter says: It is certainly true that spin contamination can be a problem in DFT, unless one does restricted DFT, which is not usually done. The problem is that really one needs a multireference wavefunction with all possible spin functions included variationally in order to get proper reaction paths. This brings us back to *ab initio* methods however, since multireference DFT does not make sense to me.

(UNCLEAR as to state of progress)

Another problem with many functionals when used in mapping reaction PESs, is the well-known electron "self interaction error." It was suggested that methods already exist for correcting this error in some functionals, but the consensus seemed to be that more work needs to be done on this topic.

Emily Carter adds: Yes this is the problem with radicals. All DFT methods without full exact exchange, i.e., all of them, will have this problem. More work needs to be done on this topic.

(LONG-TERM GOAL)

For crystals under very high pressures or pressure waves, it was said that a better description of the excited electronic states is needed within DFT, or at least the excitation energies into these states. This problem with predicting accurate excitation energies is also related, at least in part, to the well-known problem of errors in the eigenvalues associated with the Kohn-Sham unfilled orbitals (or bands) which tend to have incorrectly small values.

Report of Focus Group 2

(reported by Betsy Rice)

The task of the discussion groups was to determine what can be done using currently available tools and to identify critical "deficiencies" in the models/tools that deserve attention in order to further the methodology. The currently used methods of energy optimization with empirical force fields cannot always identify the correct crystal structures. However, if the X-ray model is used as the packing probe, the smallest lattice energy indicates the correct structure ~80% of the time. It is expected that the predictive power of these methods will further increase after the current massive re-parameterization of force fields by the Ammon group is finished.

Sources of failure of *ab initio* crystal prediction were identified:

1. Failure to identify the global minimum (ranking of candidate crystals)
 - a. Inadequate configuration space search
 - b. Rigid molecule approximation when applied to floppy molecules
 - c. Lattice energy calculations are not accurate enough.
2. Kinetic thermodynamic problem

Recommendations for addressing these issues using currently available computational tools

Recommendation to address issue 1.a

- This problem has become less important as modern lattice optimization programs can sample huge numbers of structures within reasonable computer time. Although some unusually complex crystal structures ($Z' > 1$, disordered, etc.) cannot be explicitly and accurately found with current searches, the searches are likely to generate simpler, closely related structures of comparable energy.

Recommendation to address issues 1.b

- Perform local-density approximation (LDA), since LDA is known to give accurate geometries, or *ab initio* calculations of various conformers of isolated molecule. This would include geometry optimizations for stable structures and a few single-point calculations for structures representing intermediate geometries for inter-conversion from one conformer to another. The number of conformers/structures to be considered depends on how high are conformers' energies above the global minimum compared to the lattice energy of a given crystal. LDA is proposed here as a very fast method since hundreds of calculations during the optimization of geometries of large molecules including conformers will have to be performed. However, LDA energies are rather inaccurate.
- Use the molecular structures of the isolated conformers obtained in this way to generate candidate crystal structures (e.g., MOLPAK program search) and subsequent energy minimization assuming simple analytic potential energy function.

- Rank candidates in energy using both lattice energies and energies of isolated molecules.
- Perform *ab initio* monomer calculations at LDA geometries for a number of most promising candidates and refine the energy rankings by replacing LDA monomer energies by *ab initio* ones. Furthermore, *ab initio* full geometry optimization can be performed for a couple of top candidates that represent local minima to refine also monomer geometries, and the MOLPAK search can then be repeated.
- Alternatively, periodic boundary conditions (PBC) Moeller-Plesset perturbation theory in second order (MP2) calculations can be performed for a few most promising candidates.

Alternative recommendation to address issue 1.b

- Investigate effect on packing due to inclusion of limited flexibility (i.e., flexibility in only a few degrees of freedom chosen based on chemical structure) of the “building block” molecule – A flexible force field as a function of small Cartesian displacements of each atom from its equilibrium position can be obtained from the energy second derivative matrix calculated from isolated molecule calculations. This will be able to reflect the small deviations in conformation, such as distortions of covalent bonds to hydrogen (e.g. making -NH₂ pyramidal) or rotation of nitro groups, which are induced by the crystal packing to improve hydrogen bonding energies or allow denser packings. The effects of flexibility are also under development by the Ammon group. Their approach is to use intramolecular energy differences (from PM3 semi-empirical or Dreiding molecular mechanics calculations) plus intermolecular energies to provide a total energy for the packing process. One aspect not being addressed at present is the refinement of crude structures by minimization of the lattice plus intramolecular energies. This will require at least significant modification to existing software and may require development of a new suite of programs.

Recommendation to address issue 1.c

- Improve the description of van der Waals interactions by using better asymptotic constants obtained from *ab initio* calculations.
- Get experimental sublimation energies in order to compare experiment with calculations and improve empirical potentials, in particular for multi-nitro and multi-nitramino compounds.

Recommendation to address issue 2

- The existence of polymorphism shows that thermodynamically metastable crystal structures are observed. Investigate methods that the pharmaceutical industry uses to experimentally identify possible polymorphs and assess their relative thermodynamic stability. (They are looking to computational predictions as back up for these searches, to help increase confidence that all long-lived polymorphs have been found. There are cases when the more stable polymorph has only been found late in the development process, and a few disasters when it has been found in the manufacturing process).
- Assess effect of free energy using quasi-harmonic calculation; do free energy minimization; if unstable, do Molecular Dynamics on candidate crystals. However, the consensus was that considerations of free energies make little difference from the point of view of crystal structure predictions, as this only reshuffles the relative stability when there are many

possible crystal structures within the energy gap of possible polymorphism. It does, however, improve the realism of the thermodynamic stability comparison.

Recommendation on the use of PBC codes:

- Current DFT implementations are not reliable for describing the interactions between molecules within an organic crystal. Besides, energy minimizations needed to find the global minimum would be too time-consuming with these methods.
- MP2 will give reliable predictions but is more expensive than DFT. As stated above, MP2 can be used to compute lattice energies for a number of close-lying structures obtained by other methods. Unfortunately, the size of basis set and level of theory required to properly calculate the dispersion energy will make this a considerable challenge. Underestimating the dispersion energy will tend to overestimate cell volumes, which will give errors that are unlikely to be comparable between different hypothetical structures.

Recommendations for future research to advance *ab initio* crystal prediction

Recommendation to address issue 1.c

- Increase accuracy of atom-atom potentials using symmetry-adapted perturbation theory (SAPT) of intermolecular interactions.
- Develop more realistic potential energy descriptions to include multi-body effects for use in packing calculations.
- Investigate transferability of the potentials.
- Couple DFT, tight-binding or MNDO code with the packing code to use self-consistent electrostatics in the solid. This would allow an improved electrostatic model that was consistent with both the internal configuration of the molecule as well as the crystalline environment.
- Make problems available to people who are working on problem of better descriptions of dispersion.
- Develop gradients for MP2/PBC.
- Develop DFT functionals that can be used for molecules of interest in PBC crystal lattice calculations with plane wave or atomic basis sets.

Recommendation to address issue 2

- Investigate ways to simulate nucleation/crystal growth to establish which energetically feasible crystal structures are kinetically favored. Obtain experimental information to validate methods

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Workshop on Tools for Condensed Phase Computational Chemistry

Clayton Hall, University of Delaware, 27-30 May 2003

PROGRAM

May 27: Registration starts at 18:00 and dinner at 19:00 in Clayton Hall.

May 28: Registration 7:30-10:00 in Clayton Hall.

DOD Programs and Needs for Computational Chemistry Packages

08:30-09:15	Betsy Rice, Cary Chabalowski, William Mattson	ARL	Army Needs for Crystal Structure and other Property Predictions
09:15-09:45	Betsy Rice	ARL	Parallelizing Molpak and Planewave
09:45-10:00	Break		
10:00-10:30	David Singh	NRL	Pseudopotential and Planewave Codes

Presentations by Experts

10:30-11:30	Krzysztof Szalewicz	U. Delaware	Intermolecular Interaction Potentials
11:30-12:30	Herman Ammon	U. Maryland	Crystal Structure Prediction for Energetic Materials
12:30-13:30	Lunch		
13:30-14:30	Sally Price	U. Coll. London	Anisotropic Atom-Atom Intermolecular Potentials in Organic Crystal Structure and Property Prediction
14:30-15:30	Emilio Artacho	Cambridge U.	Material Properties with SIESTA: Strengths, Weaknesses, and Prospects
15:30-16:00	Break		
16:00-17:00	Julian Gale	Imperial Coll.	General Utility Lattice Program
17:00-18:00	Anne Chaka	NIST	Validation of Computational Methods
18:00-19:30	Dinner		
19:30-21:00	Discussion		Possible Implementations of New Approaches by Army

May 29:

Presentations by Experts (continued)

0830-09:30	Eric Bylaska	PNNL	Materials Properties with NWChem
09:30-10:30	Richard Martin	U. Illinois	Identifying the Key Problems in Present Density Functionals
10:30-11:00	Break		
11:00-12:00	Gustavo Scuseria	Rice U.	Condensed Phase Simulations using Gaussian Orbitals and Periodic Boundary Conditions
12:00-13:00	Lunch		
13:00-14:00	Emily Carter	UCLA	Modeling Chemistry and Physics in Bulk Crystals, Surfaces, and Interfaces: What's Possible and What Can We Trust?

Group discussion: Best Ways to Proceed on Army Problems

14:00	Krzysztof Szalewicz and Bob Shaw		Summary remarks and guidelines for discussion groups
14:00-17:00	Discussion group I		Chabalowski, Byrd, Mattson, Martin, Carter, Bylaska, Scuseria, Doren, Tchoukova, Murdachaew, Sandler, Shaw
14:00-17:00	Discussion group II		Rice, Kim, Ammon, Price, Gale, Artacho, Chaka, Singh, Bukowski, Akin-Ojo, Wang, Rowe, Szalewicz
15:30-15:45	Break		
17:00-18:00	Discussion		Groups Report back with their Conclusions
18:00	Dinner		